

# Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: Analytical Py-GC/MS study

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## HIGHLIGHTS

- We promote aromatic hydrocarbon production by catalytic co-pyrolysis process.
- Co-pyrolysis temperature of 700 °C is optimal for aromatic hydrocarbon formation.
- The hydrogen to carbon effective ratio of feedstock should be adjusted to >1.0.

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## ABSTRACT

In order to promote efficient production of aromatic hydrocarbons, catalytic co-pyrolysis of corn stalk and high density polyethylene (HDPE) over HZSM-5 zeolite catalyst was performed using quantitative Py-GC/MS. For the catalytic fast pyrolysis (CFP) of HDPE, the relative content of aromatic hydrocarbons tended to increase at first and then decreased gradually. For the catalytic co-pyrolysis (co-CFP) of biomass and HDPE, the effects of co-CFP temperature and mass ratio of biomass to HDPE (biomass/HDPE ratio) on the relative content and economic potential of aromatic hydrocarbons were investigated, and the experimental results showed that the highest relative content of aromatic hydrocarbons was obtained at the temperature of 500–600 °C, whereas 700 °C was optimal when the yield of total organic pyrolysis products was taken into account. In addition, the relative contents and value index (VI) of target products remained virtually constant when the biomass/HDPE ratio was >1:1, but then increased with decreasing biomass/HDPE ratio when this mass ratio was <1:1. The hydrogen to carbon effective ratio ( $H/C_{eff}$  ratio) of feedstock should be adjusted to be >1.0 so that high relative contents and VI of aromatic hydrocarbons could be achieved.

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## 1. Introduction

Massive consumption of traditional fossil energy resources has caused serious problems and prompted considerable interest in alternative renewable energy [1,2]. As the only renewable resource that can be directly converted to liquid fuels, biomass has attracted increasing attention [3,4]. A wide array of methods has been researched to achieve high-quality liquid fuels (namely bio-oil) from lignocellulosic biomass [5,6], and one of the most promising ways is catalytic fast pyrolysis (CFP) technology that employs fast pyrolysis process and acidic catalysts. Addition of acidic catalysts can de-oxygenate bio-oil and favor the production of hydrocarbon products through catalytic cracking and refining reactions. Among various studied acidic catalysts, HZSM-5 zeolite catalyst has shown an excellent performance [7–9].

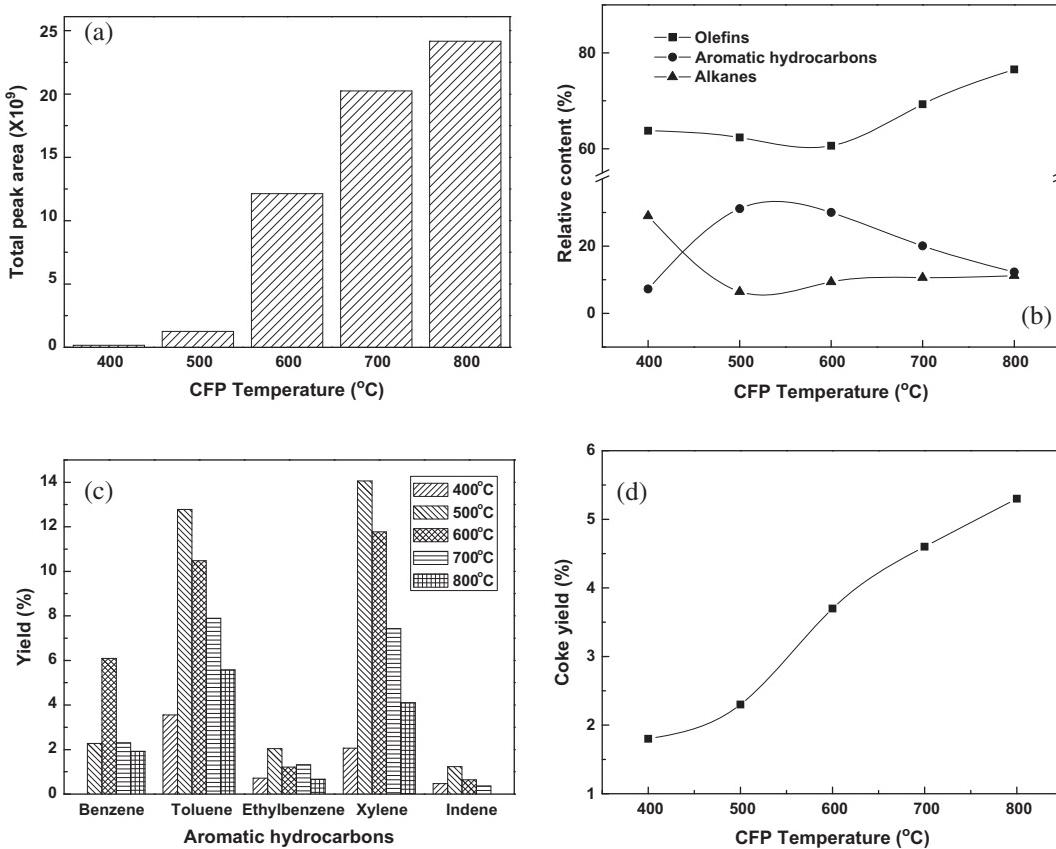
However, solid biomass is a hydrogen-deficient feedstock, thus leading to adverse impacts on hydrocarbon production from CFP process. Chen et al. [10] used a parameter called hydrogen to carbon effective ratio ( $H/C_{eff}$  ratio) to reflect the relative hydrogen content of different feedstocks. The  $H/C_{eff}$  ratio is defined as

$$H/C_{eff} = \frac{H - 2O - 3N - 2S}{C} \quad (1)$$

where H, O, N, S and C are the mole percentages of hydrogen, oxygen, nitrogen, sulfur and carbon in feedstocks, respectively. The  $H/C_{eff}$  ratio of biomass and biomass-derived feedstocks is only 0–0.3, which exhibits an extreme lack of hydrogen. Zhang et al. [11] reported the zeolite conversion of 10 biomass-derived feedstocks with different  $H/C_{eff}$  ratios, and their experimental results indicated that there was a strong correlation between the  $H/C_{eff}$  ratio of feedstock and the content of hydrocarbons. Furthermore, the content of hydrocarbons could be promoted by increasing the  $H/C_{eff}$  ratio in feeds. Catalytic co-pyrolysis (co-CFP) of biomass with another additional feedstock that has a high  $H/C_{eff}$  ratio is an

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**Fig. 1.** CFP of HDPE over HZSM-5 catalyst – effect of CFP temperature. (a) Total peak areas. (b) Relative contents of hydrocarbons. (c) Relative contents of several kinds of aromatic hydrocarbons. (d) Coke yields.

attractive approach to increase the content of hydrocarbons. Grease ( $H/C_{eff}$  ratio = ~1.5) and saturated monohydric alcohols ( $H/C_{eff}$  ratio = 2) can function as hydrogen sources and be co-fed with biomass to improve the overall  $H/C_{eff}$  ratio of feedstocks. Zhang et al. [12] found that co-CFP of biomass and methanol could give rise to a high yield of premium products over HZSM-5 catalyst. Unfortunately, the high prices of grease and alcohols seriously limit their practical use, so it is necessary to find other low-cost feedstocks.

As a common municipal solid waste, Polyethylene (PE) can potentially act as the better hydrogen supplier in co-CFP process because of its broad sources, low price and high  $H/C_{eff}$  ratio ( $H/C_{eff}$  ratio = 2). In this paper, co-CFP of corn stalk and high density polyethylene (HDPE) with HZSM-5 catalyst was carried out, and quantitative pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) was used to analyze the chemical compositions of products. The objective of this work is to evaluate the relative contents and economic potential of aromatic hydrocarbons and determine the optimal conditions during the CFP of corn stalk and PE mixtures.

## 2. Materials and methods

### 2.1. Materials

Corn stalk was supplied by a trading center in the city of Zhumadian in Henan Province, China. HDPE was collected from a company in the city of Nanjing in Jiangsu province, China. Prior to the beginning of the experiments, both corn stalk and HDPE were pulverized mechanically and sifted through a 40-mesh sieve. The proximate analysis of the corn stalk (on air-dry basis) was

9.27 wt% moisture, 71.73 wt% volatile, 6.06 wt% ash, and 12.94 wt% fixed carbon (by difference). The elemental composition of the corn stalk (on air-dry, ash-free basis) was 46.73 wt% carbon, 6.11 wt% hydrogen, 0.59 wt% nitrogen, and 46.57 wt% oxygen (by difference). Besides, the  $H/C_{eff}$  ratio of corn stalk was 0.04, and the density of HDPE was 0.97 g/cm<sup>3</sup>.

HZSM-5 zeolite catalyst (silicon-to-aluminum ratio is 50, particle diameter is 2–5 µm) used in this study was bought from the Catalyst Plant of Nankai University. The porosity and acidity characteristics of the HZSM-5 catalyst are given in Table 1. The porosity characteristic of HZSM-5 catalyst was analyzed by  $N_2$  porosimetry, and the D-R equation was used in the calculation of the surface area. The acidity characteristic of HZSM-5 catalyst was analyzed by Py-FTIR measurement. The FTIR spectrum was recorded using Bruker TENSOR27 infrared spectrometer with a range of 400–4000 cm<sup>-1</sup> at the resolution of 4 cm<sup>-1</sup>. HZSM-5 catalyst was dispersed on the thin wafers of KBr and pyridine was used as a probe. The samples were calcined under vacuo at 380 °C for 2 h, and then the adsorption of pyridine vapor was operated at room temperature for 30 min. IR spectrum was recorded and analyzed after subsequent evacuation at 200 °C.

**Table 1**  
Porosity and acidity characteristics of HZSM-5 catalyst.

Porosity characteristics ( $N_2$ porosimetry)		
Specific surface area (m <sup>2</sup> /g)	332	
Pore volume (cm <sup>3</sup> /g)	0.1925	
Acidity characteristics (Py-FTIR measurement)		
Brönsted acid sites (µmol/g)	134.3	
Lewis acid sites (µmol/g)	32.2	

**Table 2**

Comparison of CFP of biomass, HDPE, and their mixtures over HZSM-5 catalyst.

	I	II	III	IV
Experiments	CFP of biomass	CFP of HDPE	CFP of their mixtures	
Feedstock	0.50 mg powdered corn stalk samples	0.50 mg powdered HDPE samples	0.25 mg powdered corn stalk samples + 0.25 mg powdered HDPE samples, fully mixed	$\frac{I+II}{2}$
Total peak area ( $\times 10^9$ )	2.88	12.14	9.55	7.51
Relative content of hydrocarbons (%)	59.1	100.0	84.9	79.5

CFP temperature: 600 °C.

## 2.2. Pyrolysis procedure

Py-GC/MS is an important technique as it can provide the information about the properties of pyrolysis vapors. Catalytic co-pyrolysis was carried out in a CDS Pyroprobe 5200 pyrolyzer. The probe is a resistively heated element and holds an open ended quartz tube. Prior to the experiments, the quartz tube was successively filled with some quartz wool, 0.50 mg HZSM-5 catalyst, some quartz wool, 0.50 mg corn stalk and HDPE mixtures, some quartz wool, 0.50 mg HZSM-5 catalyst and some quartz wool. The HZSM-5 catalyst was placed at both sides of the feedstock and acted as fixed beds. Thus, the non-catalytic fast pyrolysis took place first and then the primary product vapors were upgraded when they passed through the catalyst layer. During the experiments, a desired pyrolysis temperature was held for 20 s with a heating rate of 20 °C/ms. High-purity helium (99.999%, Nanjing Maikesi Nanfen Special Gas Co., Ltd.) was used as carrier gas at a constant flow of 1.0 mL/min.

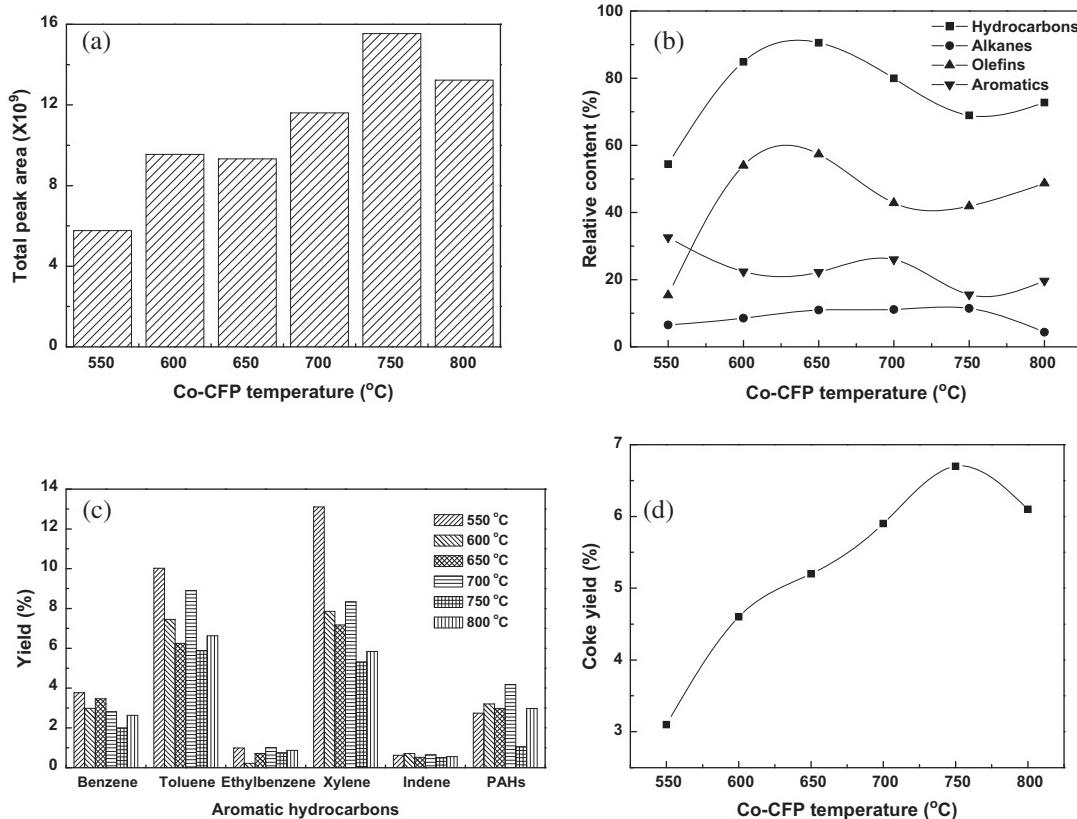
The pyrolysis vapors flowed from the quartz tube into a gas chromatography/mass spectrometry (7890A/5975C, Agilent) via the helium sweeper gas stream. The GC/MS injector temperature of 275 °C and interface temperature of 300 °C were held. The GC

separation was carried out using a capillary column named HP-5MS (30 m × 0.25 mm × 0.25 μm). A split ratio of 1:80 was used. Typical operating conditions of MS were ionization energy 70 eV, and scan per second over range electron  $m/z$  = 35–550 amu. Each experiment was repeated at least three times under the same conditions, and their average values were calculated and used for discussion.

## 2.3. Product analysis

The chromatographic peaks were discriminated and analyzed by means of the NIST MS library and other literature data [13–17]. For each chemical composition, a calibrated peak area% was achieved to represent its relative content. Besides, it was known that the products could not be collected during Py-GC/MS experiments, so the yields of total organic pyrolysis products could not be determined. However, the total calibrated chromatographic peak areas could be used to reveal the changes of product yields, because the mass of feedstock was kept exactly the same during each experiment.

The spent HZSM-5 catalyst samples were collected and dried at 120 °C for 1 h in a drying oven. Then the dried samples were put



**Fig. 2.** Co-CFP of biomass and HDPE over HZSM-5 catalyst – effect of co-CFP temperature. (a) Total peak areas. (b) Relative contents of hydrocarbons. (c) Relative contents of several kinds of aromatic hydrocarbons. (d) Coke yields.

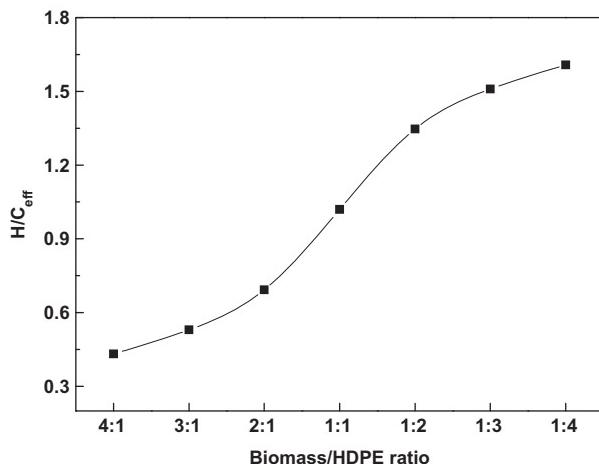


Fig. 3.  $H/C_{eff}$  ratios of feedstock under different biomass/HDPE ratios.

into a muffle furnace for combustion ( $650\text{ }^{\circ}\text{C}$ , 2 h) so that the coke yields were determined.

### 3. Results and discussion

#### 3.1. Catalytic fast pyrolysis of HDPE

CFP of biomass has been studied widely and incremental advances have been made, whereas CFP of HDPE still needs in-depth research. In this work, CFP of HDPE with HZSM-5 catalyst was conducted and the effect of CFP temperature was investigated. During each experiment, 0.50 mg powdered HDPE samples were used as feedstock in the quartz tube.

The total peak areas under different CFP temperature levels are shown in Fig. 1(a). When the CFP temperature increased from 400 to  $800\text{ }^{\circ}\text{C}$ , the yield of total organic pyrolysis products increased dramatically. The underlying reason may be that HDPE was not pyrolyzed adequately at low CFP temperatures, and its conversion was promoted at high CFP temperatures. For the same reason, the coke yield showed the same tendency (Fig. 1(d)).

When HDPE was pyrolyzed, free radical reactions with random chain scission would occur [18], resulting in the formation of olefins and alkanes. Besides, the pore system of HZSM-5 catalyst contained sinusoidal channels of  $0.51 \times 0.54\text{ nm}$  and straight channels of  $0.54 \times 0.56\text{ nm}$ , and the HZSM-5 pore diameter was similar to the dynamics diameters of benzene, toluene and xylene, so the HZSM-5 catalyst had a significant shape-selective effect on the products of aromatic hydrocarbons [19]. When the primary product vapors passed through the HZSM-5 catalyst layer, they would diffuse into the internal pores of HZSM-5 catalyst and form aromatic hydrocarbons through a common intermediate (called "hydrocarbon pool") in the HZSM-5 framework (reaction (2)) [20–25].

The relative contents of olefins, aromatic hydrocarbons and alkanes under different CFP temperatures are presented in Fig. 1(b), and detailed relative contents of several kinds of aromatic hydrocarbons, such as benzene or toluene, are shown in Fig. 1(c). CFP of HDPE was an endothermic process, so the increasing CFP temperature was beneficial for the generation of olefins and alkanes. On the other hand, reaction temperature of  $500\text{--}600\text{ }^{\circ}\text{C}$  was conducive to the formation of aromatic hydrocarbons, and a large portion of olefins and alkanes would be converted to aromatic hydrocarbons on the surface of HZSM-5 catalyst on this condition. Therefore, the relative contents of olefins and alkanes tended to decrease at first and then increase over the range of pyrolysis temperature studied, while the relative content of aromatic hydrocarbons increased to a maximum value at  $500\text{--}600\text{ }^{\circ}\text{C}$ , and then decreased gradually. Besides, CFP of HDPE with HZSM-5 catalyst did not result in the formation of polycyclic aromatic hydrocarbons (PAHs).

#### 3.2. Catalytic co-pyrolysis of biomass and HDPE

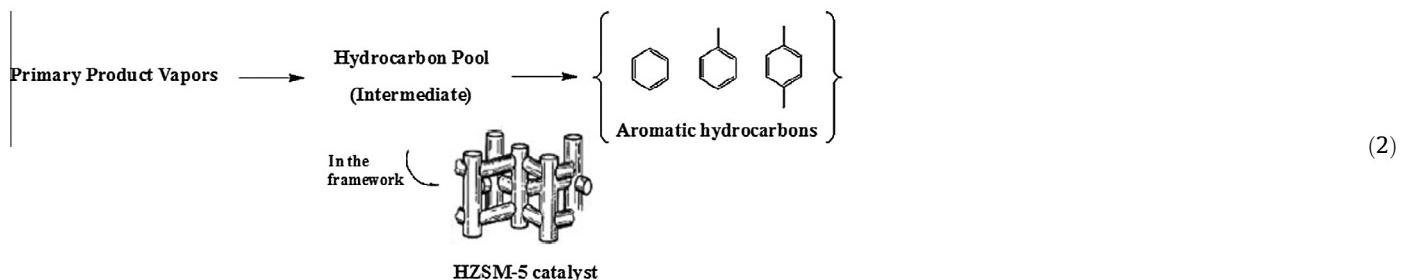
A simple comparison of CFP of biomass, HDPE and their mixtures is given in Table 2. The total peak area and the relative content of hydrocarbons of III were larger than that of IV, revealing a remarkable synergistic effect between biomass and HDPE. Co-feeding HDPE would provide hydrogen atoms for co-CFP process and increase the rate of hydrocarbon production. Meanwhile, oxygenated compounds in the corn stalk fast pyrolysis vapors could promote the chain scission and cracking of HDPE [26,27].

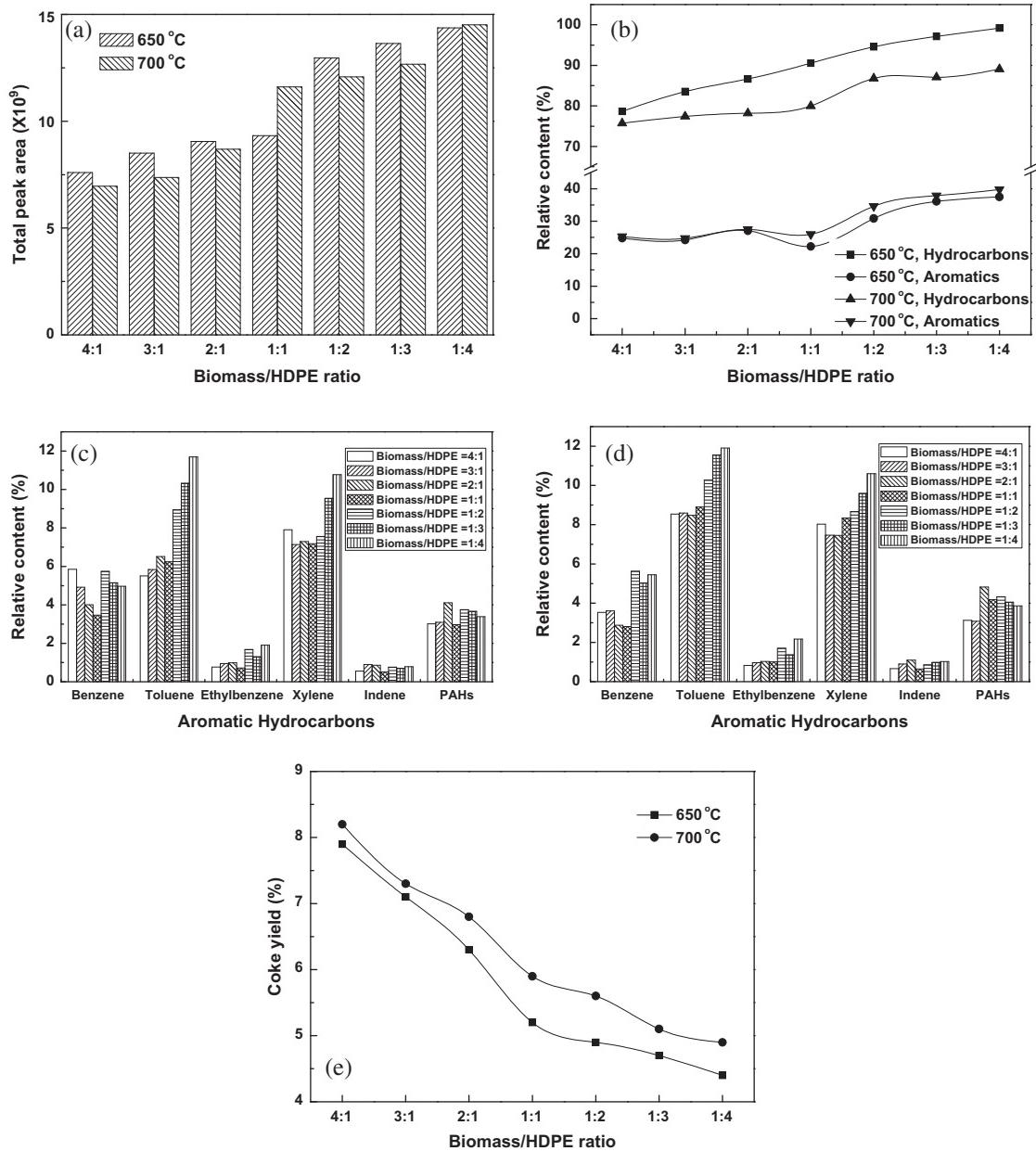
##### 3.2.1. The effect of catalytic co-pyrolysis temperature

During each experiment, 0.25 mg powdered corn stalk samples and 0.25 mg powdered HDPE samples were fully mixed and used as feedstock in the quartz tube. The co-CFP temperatures were set at  $550, 600, 650, 700, 750$  and  $800\text{ }^{\circ}\text{C}$ , respectively.

The total peak areas under different co-CFP temperatures are shown in Fig. 2(a). The yield of total organic pyrolysis products increased from  $550$  to  $750\text{ }^{\circ}\text{C}$ , and then decreased beyond  $750\text{ }^{\circ}\text{C}$ . For CFP of HDPE, the yield of total organic pyrolysis products increased dramatically with increasing temperature (see Fig. 1(a)). For CFP of biomass, the yield of total organic pyrolysis products first increased to a maximum value at  $450\text{--}550\text{ }^{\circ}\text{C}$ , and then decreased. Change of the yield of co-CFP total organic pyrolysis products might be caused by the superposition effects of aforementioned two factors. Besides, coke yield had the same varying trend (Fig. 2(d)).

The relative contents of olefins, aromatic hydrocarbons and alkanes are shown in Fig. 2(b) and (c). As can be seen, the highest relative content of aromatic hydrocarbons was obtained at the co-CFP temperature of  $550\text{ }^{\circ}\text{C}$ , but  $700\text{ }^{\circ}\text{C}$  was optimal when the yield of total organic pyrolysis products was taken into account because higher yields of both total organic pyrolysis products and aromatic hydrocarbons could be achieved on this condition. Note that polycyclic aromatic hydrocarbons (PAHs) were toxins, and special





**Fig. 4.** Co-CFP of biomass and HDPE over HZSM-5 catalyst – effect of biomass/HDPE ratio. Total peak areas. (b) Relative contents of hydrocarbons. (c) Relative contents of several kinds of aromatic hydrocarbons (650 °C). (d) Relative contents of several kinds of aromatic hydrocarbons (700 °C). (e) Coke yields.

attention should be paid to the generation of PAHs during this co-CFP process. As highly desirable compounds, aromatic hydrocarbons were selected as target products in our work. The formation of aromatic hydrocarbons came from two aspects. On the one hand, olefins and alkanes from HDPE pyrolysis could be converted to aromatic hydrocarbons. On the other hand, oxygenated organic compounds from biomass pyrolysis would suffer deoxygenation reactions and form aromatic hydrocarbons when processed through the catalyst layer.

### 3.2.2. The effect of mass ratio of biomass to HDPE (biomass/HDPE ratio)

During each experiment, the overall mass of feedstock (corn stalk and HDPE mixtures) was kept exactly 0.50 mg, and the co-CFP temperature was set at 650 or 700 °C. The  $H/C_{eff}$  ratio of feedstock increased with the decrease of biomass/HDPE ratio (see Fig. 3). When the biomass/HDPE ratio was 1:1, the  $H/C_{eff}$  ratio of feedstock was approximately 1.0.

Total peak areas under different biomass/HDPE ratios are shown in Fig. 4(a). Obviously, the total organic pyrolysis product yield increased in the studied mass ratio range. The relative contents of aromatic hydrocarbons are shown in Fig. 4(b)–(d). Co-feeding HDPE with biomass led to a pronounced increase in the relative content of hydrocarbons. The promotion of hydrocarbon production was possibly arising from the fact that a higher  $H/C_{eff}$  ratio was obtained when the biomass/HDPE ratio decreased. Besides, when the biomass/HDPE ratio was >1:1, the relative contents of aromatic hydrocarbons remained virtually constant, and then increased with decreasing biomass/HDPE ratio when this mass ratio was <1:1. The results revealed that the  $H/C_{eff}$  ratio would have an important impact on the relative content of aromatic hydrocarbons only when it exceeded a certain value of approximate 1.0. Wang et al. [28,29] also found that the yield of usable products from zeolite conversion is a function of  $H/C_{eff}$  ratio and there was an inflection point. Besides, from Fig. 4(e) we can see that the coke yield decreased with the increasing of  $H/C_{eff}$  ratio.

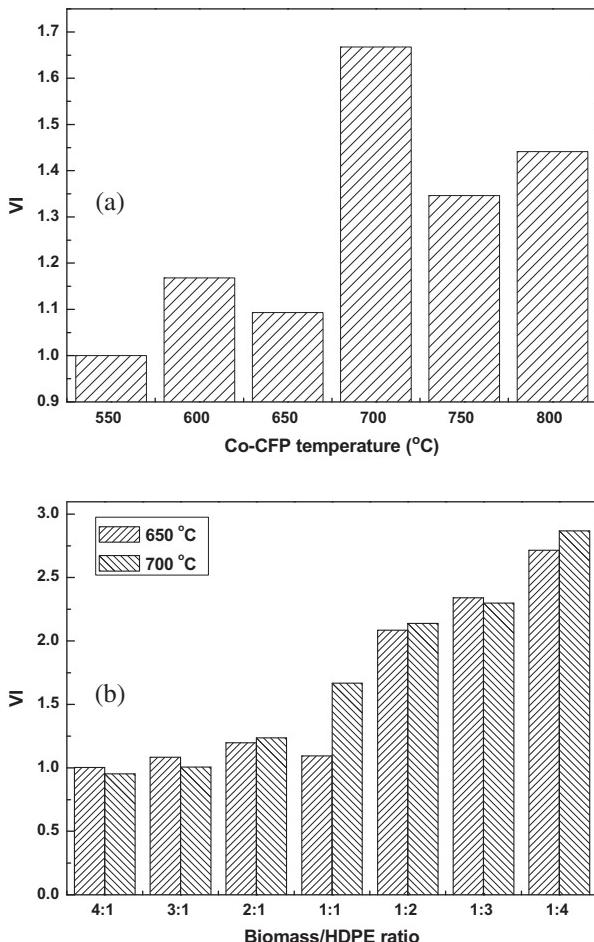


Fig. 5. VI. (a) Effect of co-CFP temperature. (b) Effect of biomass/HDPE ratio.

### 3.2.3. Economic analysis of target products

The economic potential of aromatic hydrocarbons was also studied, and the prices of aromatic hydrocarbons were based on the following values: 8600 yuan/ton-benzene, 8000 yuan/ton-toluene, 13,000 yuan/ton-ethylbenzene, 8000 yuan/ton-xylene, 5500 yuan/ton-indene, 7800 yuan/ton-PAHs [30]. In order to evaluate and analyze the economic potential under different conditions, a parameter called value index (VI) was used and defined as

$$VI = \frac{S \times \sum(C_{\text{aromatic}} \times V_{\text{aromatic}})}{S_{(550^{\circ}\text{C}, \text{biomass/HDPE}=1:1)} \times \sum(C_{\text{aromatic}, 550^{\circ}\text{C}, \text{biomass/HDPE}=1:1} \times V_{\text{aromatic}})} \quad (3)$$

where  $S$  is the total peak area under a certain condition,  $S_{(550^{\circ}\text{C}, \text{biomass/HDPE}=1:1)}$  is the total peak area at the co-CFP temperature of 550 °C and the biomass/HDPE ratio of 1:1,  $C_{\text{aromatic}}$  is the relative content of a certain kind of aromatic hydrocarbons, such as benzene or toluene,  $C_{\text{aromatic}, 550^{\circ}\text{C}, \text{biomass/HDPE}=1:1}$  is the relative content of a certain kind of aromatic hydrocarbons at the co-CFP temperature of 550 °C and the biomass/HDPE ratio of 1:1, and  $V_{\text{aromatic}}$  is the price.

The analysis results are given in Fig. 5(a) and (b). When the biomass/HDPE ratio was fixed, the highest VI value was achieved at the co-CFP temperature of 700 °C. When the co-CFP temperature was fixed, the VI value increased significantly with the increase of  $H/C_{\text{eff}}$  ratio when  $H/C_{\text{eff}}$  ratio was >1.0, while the VI value remained almost constant when  $H/C_{\text{eff}}$  ratio was <1.0. Therefore, in order to promote the production of aromatic hydrocarbon in

engineering, the  $H/C_{\text{eff}}$  ratio of feedstock should be improved to be >1.0.

### 4. Conclusions

In this study, co-CFP of corn stalk and HDPE with HZSM-5 catalyst was carried out using Py-GC/MS and aromatic hydrocarbons were selected as target products. For CFP of HDPE, the relative content of aromatic hydrocarbons increased to a maximum value at 500–600 °C, and then decreased gradually. For co-CFP of biomass and HDPE, effect of co-CFP temperature and biomass/HDPE ratio on the relative contents and VI of aromatic hydrocarbons were investigated. The results illustrated that the highest relative content of aromatic hydrocarbons was obtained at the co-CFP temperature of 550 °C, but 700 °C was optimal when the yield of total organic pyrolysis products was taken into account. Besides, when the biomass/HDPE ratio was >1:1, the relative contents and VI of aromatic hydrocarbons remained virtually constant, and then increased with decreasing biomass/HDPE ratio when this mass ratio was <1:1. In order to promote the formation of aromatic hydrocarbons, the  $H/C_{\text{eff}}$  ratio of feedstock should be improved to be >1.0.

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